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Articles

First Conventional Syntheses and Isolation of Bis(naphthalene)metal(0) Complexes. Structural Characterization of V(η^6-$C_{10}H_8$)$_2$[1]

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Reactions of alkali-metal naphthalenides with $VCl_3(THF)_3$, $CrCl_3(THF)_3$, $MoCl_3(THF)_3$, and $MoCl_4(THF)_2$ in THF provided up to 29%, 24%, 20%, and 17% yields of the respective bis(naphthalene)metal(0) complexes. These highly reactive “naked” early-transition-metal atom reagents were accessible previously as pure substances only from metal atom reactions carried out in specialized apparatus available to few chemists. The nature of bis(naphthalene)vanadium(0) has been confirmed by a single-crystal X-ray structural characterization. These results provide another indication that the arene radical anion route is an important general strategy for the synthesis of homoleptic transition-metal arene complexes.

Homoleptic (naphthalene)metal(0) complexes offer exciting new possibilities in chemical syntheses owing to the reactivity and high lability of the naphthalene ligands as well as their ability to function as strong reducing agents. The remarkable ease with which one or both naphthalene rings may be displaced by a variety of small molecules is known as the “naphthalene effect”[2] and suggests that these substances may have general utility as “naked” metal atom reagents in early-transition-metal chemistry. Limited studies on the reactivity patterns of bis(naphthalene)chromium(0)[2−5] and its molybdenum analog[6] have often emphasized their use as storable sources of otherwise highly reactive “spin paired” atoms of chromium and molybdenum, respectively. However, extensive studies on the chemical properties of these and related species have been severely hampered by their relative inaccessibility. All previous routes to *isolated* examples of these compounds have required specialized metal atom reactor equipment, which is not widely available to many chemists and employs procedures that are not easily scaled up.[7]

Over 30 years ago Fischer et al. reported on the first synthesis of a homoleptic transition-metal naphthalene species, $[Ru(C_{10}H_8)_2]^{2+}$, isolated as the PF_6^- salt.[8] This compound was obtained by the classic Fischer−Hafner synthesis of bis(arene)metal compounds[9] and remains the sole example of a bis(naphthalene)metal complex prepared by this method. Shortly thereafter it was claimed that solutions of bis(naphthalene)metal complexes of vanadium and chromium could be obtained by lithium naphthalenide reductions of the appropriate metal trichlorides in THF.[10] These species were only detected by EPR spectroscopy and were not isolated or unambiguously identified by their chemical properties. Indeed, in 1977 when the first bona fide samples of $Cr(C_{10}H_8)_2$ were isolated from the interaction of chromium atoms with excess naphthalene, it was noted that the lithium naphthalenide reductions of $CrCl_3(THF)_3$ gave only partially hydrogenated species such as bis(η^6-tetralin)chromium(0) as isolated products[11] and *“failed to yield the elusive naphthalene sandwich compound.”*[12]

Recently, we have shown for the first time that reductions of early-transition-metal halides by *conventionally* generated alkali-metal naphthalenides yielded isolable bis- or tris(naphthalene)metal species, i.e., $[Ti(\eta^4\text{-}C_{10}H_8)_2(SnMe_3)_2]^{2-}$ [13] and $[Zr(\eta^4\text{-}C_{10}H_8)_3]^{2-}$,[14] respectively. Since potassium[15] and magnesium atom[6] reductions of mixtures of naphthalene or methyl-substituted naphthalenes and transition-metal halides in ether solvents gave isolable bis(naphthalene)metal(0)

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(1) Highly Reduced Organometallics. 43. Part 42: Barybin, M. V.; Pomije, M. K.; Ellis, J. E. *Inorg. Chim. Acta*, in press.

(2) (a) Kündig, E. P.; Perret, C.; Spichiger, S.; Bernardinelli, G. *J. Organomet. Chem.* **1985**, *286*, 183. (b) Basolo, F. *New J. Chem.* **1994**, *18*, 19. (c) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396.

(3) Kündig, E. P.; Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 912.

(4) Elschenbroich, C.; Möckel, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 870.

(5) (a) Kündig, E. P.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1980**, 991. (b) Bush, B. F.; Lynch, V. M.; Lagowski, J. J. *Organometallics* **1987**, *6*, 1267. (c) Bush, B. F.; Lagowski, J. J. *Organometallics* **1988**, *7*, 1945.

(6) Thi, N. P. D.; Spichiger, S.; Paglia, P.; Bernardinelli, G.; Kündig, E. P.; Timms, P. L. *Helv. Chim. Acta* **1992**, *75*, 2593.

(7) Klabunde, K.; Timms, P. L.; Skell, P. S.; Ittel, S. D. *Inorg. Synth.* **1979**, *19*, 59. (b) Young, D.; Green, M. L. H. *J. Appl. Chem. Biotechnol.* **1975**, *25*, 641.

(8) Fischer, E. O.; Elschenbroich, C.; Kreiter, C. G. *J. Organomet. Chem.* **1967**, *7*, 481.

(9) Elschenbroich, C.; Salzer, A. *Organometallics, A Concise Introduction*, 2nd ed.; VCH: Weinheim, Germany, 1992; pp 343−352.

(10) Henrici-Olivé, G.; Olivé, S. *J. Am. Chem. Soc.* **1970**, *92*, 4831.

(11) See footnote 4 of ref 4.

(12) See introductory comments in ref 5a. See also: Essler, H. G. Dissertation, Technische Universität München, 1960.

(13) Ellis, J. E.; Blackburn, D. W.; Yuen, P.; Jang, M. *J. Am. Chem. Soc.* **1993**, *115*, 11616.

(14) Jang, M.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1973.

(15) (a) Hawker, P. N.; Kündig, E. P.; Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1978**, 730. (b) Hawker, P. N.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1123.

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complexes or methyl substituted versions thereof, we felt that it was important to determine whether our conventional naphthalenide route would also yield these potentially quite useful substances in pure form. We now report on our results for vanadium, chromium, and molybdenum.

Experimental Section

General Procedures and Starting Materials. All operations were performed under an atmosphere of 99.9% argon or 99.5% carbon monoxide, further purified by passage through columns of activated BASF catalyst and molecular sieves. Also, the CO was passed through a column of Ascarite, which is a trade name for a self-indicating sodium hydroxide nonfibrous silicate formulation, for the quantitative absorption of CO_2. Similar products used by microanalysts should provide satisfactory results. All connections involving the gas purification systems were made of glass, metal, or other materials impermeable to air.[16] Solutions were transferred via stainless steel double-ended needles (cannulas) whenever possible. Standard Schlenk techniques were employed with a double-manifold vacuum line.[16-19] Commercial grade PF_3 (Pennwalt Ozark Mahoning) was purified by passage through two -78 °C traps and two columns of 4 Å molecular sieves and subsequent isolation at -196 °C in a 1 or 2 L gas storage flask. The PF_3 was then subjected to two freeze−pump−thaw cycles to remove O_2 and other noncondensable gases. Naphthalene was sublimed *in vacuo* before use, and literature procedures were used to prepare $VCl_3(THF)_3$,[20] $CrCl_3(THF)_3$,[20] $MoCl_3(THF)_3$,[21] and $MoCl_4(THF)_2$.[21] Alumina was activated by heating to 260 °C in a tube furnace under a flow of dry argon gas until almost all moisture was removed. Solvents were freed of impurities by standard procedures and stored under argon. Unless otherwise stated, other reagents were obtained from commercial sources and freed of oxygen and moisture before use. Solution infrared spectra were recorded on a Mattson Galaxy 6021 FTIR spectrometer with samples sealed in 0.1 mm NaCl or CaF_2 cells. Nujol (mineral oil) mulls of air-sensitive compounds for IR spectra were prepared in a Vacuum Atmospheres Corp. drybox. NMR samples were sealed into 5 mm tubes and were analyzed on a Varian Unity 300 or 500 spectrometer. Samples for EPR spectra were prepared in the glovebox and placed in quartz tubes sealed with septa and Parafilm. The data were recorded using an IBM-Bruker ESP-300 spectrometer. EPR spectra were referenced to the standard DPPH, 2,2-bis(4-*tert*-octylphenyl)-1-picrylhydrazyl, which was used as received from a commercial source. Ion spray mass spectra were obtained with a Sciex API III instrument. UV/vis data were obtained with a Cary-17D spectrometer using a 1 cm path length cell modified to allow sample transfer on a Schlenk line. Melting points are uncorrected and were obtained for samples in sealed capillary tubes with a Thomas-Hoover Uni-Melt, Model No. 6427-H10. Microanalyses were carried out by H. Malissa and G. Reuter Analytische Laboratorien, Lindlar, Germany.

$[V(C_{10}H_8)_2]$ (1). Via Alumina Oxidation of $[V(C_{10}H_8)_x]^-$. A solution of $NaC_{10}H_8$ was prepared by stirring sodium metal (1.00 g, 43 mmol), cut in small pieces (*ca.* 2−4 mm on an edge), and naphthalene (6.93 g, 54.1 mmol) in 200 mL of THF for 5 h at room temperature in a Morton flask equipped with an overhead stirrer. The $NaC_{10}H_8$ solution was then cooled to -70 °C. A slurry of $VCl_3(THF)_3$ (4.00, 10.7 mmol) in 150 mL of THF was cooled to -70 °C and added via cannula to the cold sodium naphthalenide solution with efficient stirring. An additional 100 mL of cold (-70 °C) THF was added to help dissolve components in the reaction mixture. The resulting brown solution was allowed to slowly warm to 0 °C over 12 h with constant stirring. Twenty-five grams of alumina was added by bent Schlenk tube with rapid stirring. The reddish slurry was stirred for 2 h at 0 °C and then filtered through a medium-porosity frit containing a 3 cm column of alumina. THF was removed *in vacuo* from the maroon filtrate, giving a deep maroon solid, which was pumped on at 10^{-5} Torr for 24 h at 20 °C to remove excess naphthalene. The residue was then recrystallized from toluene/pentane at -78 °C, resulting in 0.94 g (29% yield) of pure microcrystalline maroon **1**. Mp: 135 °C dec. IR: ν(C=C ring) region (mineral oil mull) 1597 cm^{-1}. Anal. Calcd for $C_{20}H_{16}V$: C, 78.17; H, 5.25. Found: C, 77.80; H, 4.98. UV−vis (THF): 366 nm, $\epsilon = 1209$ L mol^{-1} cm^{-1}. MS (ion spray, THF solution, positive radical): *m*/*e* 307.0, parent ion. EPR (3 mM THF solution, room temperature, reference DPPH; $g = 2.0036$): $g = 1.9884$, eight-line pattern, $A = 66$ G.

(1) Via PF_3 Oxidation of $[V(C_{10}H_8)_x]^-$. A solution of sodium naphthalenide was made as described above from sodium (0.62 g, 27 mmol) and naphthalene (5.15 g, 40.2 mmol) in 100 mL of DME. A cold (-60 °C) slurry of $VCl_3(THF)_3$ (2.50 g, 6.7 mmol) in 125 mL of DME was then added to the cold $NaC_{10}H_8$ solution via cannula. It was stirred at -60 °C for 2.5 h, and then the reaction vessel was evacuated until evolution of dissolved argon gas nearly ceased. Phosphorus trifluoride (*ca.* 3.6 g, 42 mmol) was then introduced from a 1 L gas storage flask. The resulting reddish brown solution was warmed to 0 °C with rapid stirring over 12 h. It was then filtered to give a deep red filtrate. Following removal of all solvent *in vacuo*, naphthalene was removed by sublimation at 30 °C and 5×10^{-2} Torr. Low-temperature (-78 °C) recrystallization of the residue from THF/pentane gave a product, 0.39 g (19% yield, based on $VCl_3(THF)_3$), which was spectroscopically identical with genuine **1**. Mass and IR spectra of the product showed no evidence for any incorporation of PF_3.

$[Cr(C_{10}H_8)_2]$ (2). A solution of $LiC_{10}H_8$ was prepared by stirring lithium metal (0.254 g, 37 mmol) and naphthalene (6.16 g, 48.0 mmol) in 150 mL of THF at room temperature for 5 h. This solution was then cooled to -70 °C with mechanical stirring. A solution/slurry of $CrCl_3(THF)_3$ (4.50 g, 12.0 mmol) and naphthalene (6.16 g, 48.0 mmol) in 200 mL of THF at -70 °C was added to the efficiently stirred cold $LiC_{10}H_8$ solution. During this addition the reaction mixture changed from a deep green to a dark brown. The mixture was stirred at -70 °C for 3 h and then slowly warmed to 0 °C over an 18 h period with constant stirring. Following filtration, all solvent was removed *in vacuo*. The resulting residue was taken up in toluene (*ca.* 400 mL). Following filtration, toluene was removed *in vacuo*, providing a brown solid. This was triturated with 200 mL of cold (-78 °C) pentane and dried *in vacuo*. The product was evacuated at 10^{-5} Torr for 48 h at room temperature to remove additional free naphthalene. Recrystallization of the residue from toluene/pentane at -78 °C gave 1.25 g (35% yield) of deep purple-black **2**, which was free of unreacted naphthalene and gave NMR spectra in excellent agreement with those previously reported.[22] ^1H NMR (300 MHz, C_6D_6 25 °C): δ 4.37 (m), 5.28 (m), 6.92 (m) ppm. ^{13}C NMR (75.5 MHz, C_6D_6, 25 °C): δ 74.8, 77.6, 89.3, 123.0, 133.9 ppm.

$[Mo(C_{10}H_8)_2]$ (3). From $MoCl_4(THF)_2$. A deep green solution of $LiC_{10}H_8$ was prepared by transferring 150 mL of

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(16) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(17) Herzog, S.; Dehnert, J.; Luhder, K. In *Technique of Inorganic Chemistry*; Johassen, H. B., Ed.; Interscience: New York, 1968; Vol. 7, pp 119−149.

(18) Kramer, G. W.; Levy, A. B.; Midland, M. M. In *Organic Synthesis via Boranes*; Brown, H. C., Ed.; Wiley: New York, 1975; Chapter 9.

(19) Wayda, A. L., Darensbourg, M. Y., Eds. *Experimental Organometallic Chemistry*; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

(20) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

(21) Dilworth, J. R.; Richards, R. L. *Inorg. Synth.* **1980**, *20*, 119.

(22) (a) Elschenbroich, C.; Möckel, R.; Massa, W.; Birkhahn, M.; Zenneck, U. *Chem. Ber.* **1982**, *115*, 334. (b) Desobry, V.; Kündig, E. P. *Helv. Chim. Acta* **1981**, *64*, 1288.

THF into a flask containing Li metal (0.337 g, 48.6 mmol), cut into 20−30 small pieces, $C_{10}H_8$ (9.24 g, 72.0 mmol), and a glass covered stirbar. After the mixture was stirred for 5 h at room temperature, it was cooled to −60 °C. Then a cold (−60 °C) solution/slurry of $MoCl_4(THF)_2$ (4.59 g, 12.0 mmol) and $C_{10}H_8$ (6.16 g, 48.0 mmol) was added to the cold (−60 °C) $LiC_{10}H_8$ solution. The mixture was warmed to −20 °C for a period of 15 h while being efficiently stirred. Thereafter, a red-brown solution was filtered at room temperature, and all the THF was removed *in vacuo*. The resulting brown solid was taken up in 150 mL of toluene and filtered. The filter cake was rinsed with toluene until the washings were colorless. The toluene was removed to provide a brown solid from which excess naphthalene was removed by sublimation (10^{-5} Torr, 25 °C). The remaining dark solid was recrystallized from toluene/pentane at −78 °C to give 0.71 g (17% yield) of **3** as lustrous dark violet crystals. The compound is not very soluble in toluene (approximately 5 g/L). ^1H NMR (300 MHz, C_6D_6, 25 °C, [AA′BB′] pattern): δ 4.68 (m, H2, H3), 5.02 (m, H1, H4), 6.56 (m, H5, H8), 6.77 (m, H6, H7) ppm. ^{13}C NMR (75.5 MHz, C_6D_6, 25 °C): δ 72.5 (d, $^1J_{H-C} = 163$ Hz, C1, C4), 78.3 (d, $^1J_{H-C} = 165$ Hz, C2, C3), 92.5 (s, C9, C10), 121.4 (d, $^1J_{H-C} = 161$ Hz, C6, C7), 131.1 (d, $^1J_{H-C} = 159$ Hz, C5, C8). These spectra are very similar to those reported by Kündig et al.[6] and indicate the absence of free ligand or other impurities in the sample. The numbering of the C,H atoms in naphthalene is identical with that used previously.[14] Our assignments of the hydrogen resonances for the unbound ring are different from those of Kündig et al.[6] and are based on a heteronuclear $^1H-^{13}C$ multiple quantum correlation (HMQC) spectrum of **3**. This spectrum established that the carbon resonances at 131 (C5, C8) and 121 (C6, C7) ppm correlate to hydrogen resonances at 6.56 and 6.77 ppm, respectively. The assignments of the carbon resonances were established unambiguously in the prior work of Kündig and co-workers.[6,22b]

From $MoCl_3(THF)_3$. A cold (−70 °C) bright orange solution of $MoCl_3(THF)_3$ (5.02 g, 12.0 mmol) and naphthalene (6.16 g, 48.0 mmol) in THF (200 mL) was transferred to a cold (−70 °C) deep green solution of $LiC_{10}H_8$, prepared from Li (0.254 g, 37 mmol) and $C_{10}H_8$ (6.16 g, 48.0 mmol) in THF (150 mL). The resulting mixture was warmed to −20 °C for a period of 15 h while being efficiently stirred. After the workup, analogous to that described above, followed by sublimation of free naphthalene (10^{-2} Torr, 25−35 °C) and recrystallization (toluene/pentane, −78 °C) of the product, 0.83 g (20% yield) of pure **3** was obtained. NMR spectra were identical with those described above and indicated the absence of free naphthalene in the sample.

X-ray Structure Determination of 1. Heptane was carefully layered on and allowed to diffuse through a nearly saturated toluene solution of **1** at −30 °C. After 14 days, deep red, almost black prisms had formed. A crystal was selected and mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Crystal data and details of the measurement are summarized in Table 1. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 49 carefully centered reflections in the range $10.00 < 2\theta < 28.00°$, correspond to a monoclinic cell. On the basis of systematic absences of $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$) and the successful solution and refinement of the structure, the space group was determined to be $P2_1/n$ (No. 14). The data were collected at a temperature of −96 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 64.0°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.00° with a takeoff angle of 2.8°. Scans of $(1.00 + 0.35 \tan \theta)°$ were made at speeds ranging from 0.9 to 8.2°/min (in ω). Moving-crystal−moving-counter background measurements were made by scanning an additional 25% above and below the scan range. The counter aperture consisted of a variable horizontal slit with a width ranging from 2.0 to 2.5 mm and a vertical slit set to 2.0 mm. The diameter of the incident beam collimator was 0.7 mm, and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector. Of the 3966 reflections that were collected, 2470 were unique ($R_{int} = 0.031$); equivalent reflections were merged. The intensities of three representative reflections that were measured after every 70 min of X-ray exposure time remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). An empirical absorption correction, using the program DIFABS,[23] was applied, which resulted in transmission factors ranging from 0.82 to 1.26. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient $0.355\,88 \times 10^{-6}$).

Table 1. Summary of Crystal Data and Intensity Measurements for 1

A. Crystal Data	
formula	$C_{20}H_{16}V$
fw	307.29
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	8.516(8)
b, Å	7.917(3)
c, Å	10.921(4)
β, deg	109.15(8)
V, Å^3	696(2)
Z	2
D_{calcd}, g cm^{-3}	1.467
cryst dimens, mm^3	0.50 × 0.50 × 0.45
temp, °C	−96
$F(000)$	318
B. Measurement of Intensity Data	
diffractometer	Enraf-Nonius CAD-4
radiation	Mo Kα ($\lambda = 0.710\,69$ Å)
monochromator	graphite
μ(Mo Kα), cm^{-1}	6.78
2θ limits, deg	10.00−28.00
final no. of variables	101
no. of observns	1735 ($I > 2.0\sigma$(I))
residuals: R, R_w [a]	0.052, 0.063
GOF [b]	2.23

[a] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o/\sigma^2(F_o^2)$. $R = (\sum||F_o| - |F_c||/\sum|F_o|)$, and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2)]^{1/2}$. [b] GOF $= [\sum(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

The structure was solved by direct methods.[24,25] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1735 observed reflections ($I > 2.00\sigma(I)$) and 101 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors shown in Table 1. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin \theta)/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.48 and −0.30 e/Å^3, respectively. Neutral atom scattering factors were taken from literature values.[26] Anomalous dispersion effects were included in F_c;[27] the values for $\Delta f'$ and $\Delta f''$ were taken from tabulated values.[26] All calculations were performed using the TEXSAN[28] crystallographic software package of Molecular Structure Corp.

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(23) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(24) Gilmore, G. D. *J. Appl. Crystallogr.* **1984**, *17*, 42.

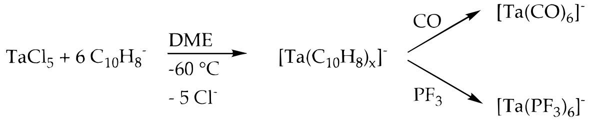
(25) Buerskens, P. T. *Direct Methods for Difference Structures*; Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed, Nijmegen, The Netherlands.

(26) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2 and 2.3.1.

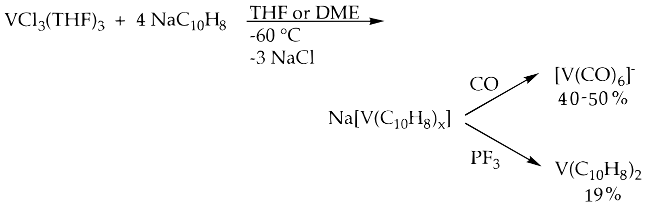
(27) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(28) TEXSAN Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, 1985.

Scheme 1



Scheme 2

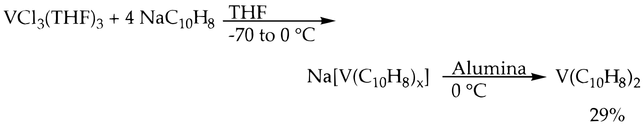


Results and Discussion

Synthesis of $V(C_{10}H_8)_2$. Bis(naphthalene)vanadium(0) was originally isolated by Kündig and Timms from the condensation of vanadium atoms in a cold methylcyclohexane–tetrahydrofuran solution of naphthalene.[3] Although the yield of product was unspecified, it gave correct analysis for the proposed composition and had an EPR spectrum which was "similar though not identical to that reported by Henrici-Olivé."[10] To our knowledge, no other information on this substance has been published to date, although Kündig and Timms stated in their original communication that "the compound promises to be an excellent starting material for preparing other zero-valent vanadium compounds."[3] On this basis we felt that the development of a conventional route to this potentially valuable substance would be useful, although our first synthesis of this material was accidental!

Earlier we had shown that naphthalenide-mediated reductions of $TaCl_5$ provided an intermediate, $[Ta(C_{10}H_8)_x]^-$, which readily combined with CO or PF_3 at low temperatures to yield the corresponding $[TaL_6]^-$ (L = CO, PF_3), as shown in Scheme 1.[29a] While the analogous reaction with $VCl_3(THF)_3$ also gave 40–50% yields of $[V(CO)_6]^-$ following carbonylation,[1] the corresponding reaction with PF_3 yielded none of the desired $[V(PF_3)_6]^-$, but only a non-PF_3-containing product that proved to be pure $V(C_{10}H_8)_2$ (**1**)! These reactions are summarized in Scheme 2. Thus, we believe the intermediate (naphthalene)vanadate, which is presently under investigation in this laboratory, was preferentially oxidized by PF_3 to provide only **1** on workup. The best route we presently have to **1** involves oxidation of the intermediate by alumina. This procedure is similar to that previously employed by Hawker and Timms to oxidize related (arene)vanadates to neutral bis(arene)vanadium species obtained by their "potassium atom" route to bis(arene)metal complexes.[15] Although they did not prepare **1** by this method, the closely related bis(1-methylnaphthalene)vanadium(0) was isolated, doubtlessly as a mixture of isomers, in 25% yield by this procedure. Our route, summarized in Scheme 3, gave a similar 29% isolated yield of pure **1**. On addition of alumina to the deep brown reaction mixture containing the (naphthalene)vanadate, the color rapidly changed to the deep red hue characteristic of solutions of **1**. Although we have not optimized the conditions for the synthesis of **1** presently, preparations using magnetic instead of mechanical stirring generally provided lower yields (*ca.* 20%). One attempt employed 1,2-dichloroethane as the oxidizing agent instead of alumina, but only a 12% yield of **1** was obtained. Since 40–50% yields of $[V(CO)_6]^-$ have been obtained by normal-pressure carbonylation of the intermediate,[1] it seems possible that similar yields of **1** may be achieved with the correct oxidant/solvent combination.

Scheme 3



Attempts to prepare **1** by the reduction of $VCl_3(THF)_3$ with *3* equiv of alkali-metal naphthalenides have been less successful. For example, two independent reductions of $VCl_3(THF)_3$ by 3 equiv of $NaC_{10}H_8$ or $LiC_{10}H_8$ in DME at −60 °C, followed by slow warming to 0 °C, provided after workup only a 7 or 13% yield, respectively, of pure **1**. It is interesting that our results in this regard closely mirror those of Hawker and Timms.[15] Their best yields of bis(arene)vanadium(0) complexes were obtained when excess potassium atoms were used in their reductions of $VCl_3(THF)_3$, which also undoubtedly involved arene radical anion mediated reactions.

Compound **1** was characterized by its infrared, UV–vis, mass, and EPR spectra, as well as by elemental analysis. A single-crystal X-ray structure determination was obtained to firmly establish the existence of this material (*vide infra*). The eight-line EPR spectrum (due to interaction of the unpaired electron with ^{51}V, which has $I = {}^7/_2$ and a natural abundance of 99.75%) compares satisfactorily with those reported originally by Henrici-Olivé[10] and later by Kündig and Timms.[3] Our preliminary investigations on the chemical properties of $V(C_{10}H_8)_2$ confirm that this highly reactive species is an excellent precursor to other zerovalent vanadium complexes. For example, in cyclohexane it quickly combines with CO at normal pressure and 20 °C to give high yields of $V(CO)_6$[29b] (eq 1). Reactions with a range

$$V(C_{10}H_8)_2 + 6CO \xrightarrow[20\ °C]{cyclohexane} V(CO)_6 + 2C_{10}H_8 \quad (1)$$

of other ligands are under examination and will be reported on at a later date.

X-ray Crystal Structure of $V(C_{10}H_8)_2$ (1). Bis(naphthalene)vanadium(0) formed single crystals that were isomorphous with those of the chromium analog, the only prior structurally characterized homoleptic (naphthalene)metal(0) species.[22] The molecular structure of **1** is shown in Figure 1 and consists of two planar and eclipsed naphthalene rings bound to vanadium in a η^6 fashion. The solid-state structures of **1** and $Cr(\eta^6\text{-}C_{10}H_8)_2$ are nearly identical. As in the case of the latter species, **1** lies on an inversion center, which is between two half-occupied metal atom positions. The disorder of the vanadium atoms is paralleled by a real but not obvious disorder in the naphthalene rings, since each portion of the rings depicted is the superposition of equal numbers of bound and free rings. Since the positions of the carbon atoms in the latter are averaged, relatively large uncertainties are present in the interatomic

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(29) (a) Ellis, J. E.; Warnock, G. W.; Barybin, M. V.; Pomije, M. K. *Chem. Eur. J.* **1995**, *1*, 521. (b) Barybin, M. V.; Ellis, J. E. Unpublished research.

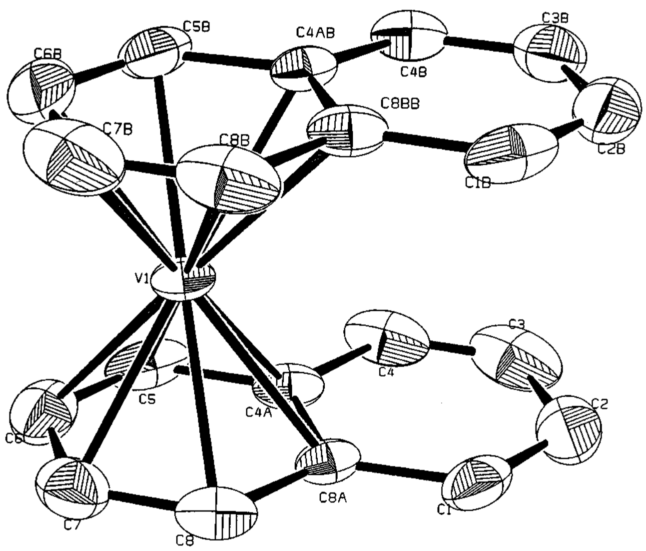
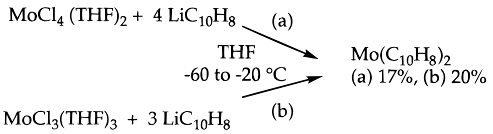


Figure 1. Molecular structure of $V(C_{10}H_8)_2$ (50% probability thermal ellipsoids). Only one vanadium atom, which is disordered equally between the two rings of each naphthalene, is shown for clarity. Selected bond lengths (Å): V−C(1), 2.173(2); V−C(2), 2.164(3); V−C(3), 2.183(2); V−C(4), 2.234(3); V−C(4A), 2.256(2); V−C(4A), 2.276(3); V−C(5), 2.198(3); V−C(6), 2.179(3); V−C(7), 2.181(3); V−C(8), 2.187(2); V−C(8A), 2.240(2); V−C(8A), 2.239(2); C(1)−C(2), 1.404(4); C(2)−C(3), 1.418(5); C(3)−C(4), 1.353(5); C(4)−C(4A), 1.417(3); C(4A)−C(5), 1.448(4); C(4A)−C(8A), 1.452(3); C(5)−C(6), 1.390(4); C(6)−C(7), 1.389(4); C(7)−C(8), 1.368(4); C(8)−C(8A), 1.422(3); C(1)−C(8A), 1.429(3).

distances for **1**. Within experimental error the average V−C distance of **1**, 2.21(4) Å, is identical with the average Cr−C distance of 2.17(2) Å found for $Cr(C_{10}H_8)_2$.[22] Similar average V−C distances have also been reported for other bis(arene)vanadium(0) species, including V(mesitylene)$_2$ (2.20(1) Å),[30] V(benzene)$_2$ (2.17 Å),[31] and $V(p\text{-}C_6H_4F_2)_2$ (2.19(2) Å).[32] The average C−C distance of 1.39(4) Å is indistinguishable from corresponding values in $Cr(C_{10}H_8)_2$ (1.41(3) Å)[22] and free naphthalene (1.41(2) Å).[33]

Synthesis of $Cr(C_{10}H_8)_2$ (2). This molecule holds a special historical position in organometallic chemistry, since it was the first homoleptic poly(arene)metal(0) species to be isolated and characterized.[3,4] Early attempts to prepare this substance by the Fischer−Hafner route failed, undoubtedly due to its high chemical reactivity and thermal instability.[4,8] While Henrici-Olivé and Olivé presented no direct evidence for the synthesis of the diamagnetic **2** by the reduction of $CrCl_3(THF)_3$ and lithium naphthalenide,[10] Timms' alternative potassium atom "wet chemical" route gave up to 36% isolated yields of bona fide $Cr(C_{10}H_8)_2$.[15] The latter synthesis almost certainly involved a reduction of $CrCl_3(THF)_3$ mediated by potassium naphthalenide. Although the latter was generated by a rather unconventional procedure, i.e., the interaction of potassium atoms with naphthalene/$CrCl_3(THF)_3$ in THF at −110 °C, there seemed to be no reason a corresponding reduction of $CrCl_3(THF)_3$ by *conventionally* generated alkali-metal naphthalenides should not work as well, despite the aforementioned reports to the contrary.[4,5a] We have not yet investigated the use of potassium naphthalenide in this reaction, but lithium and sodium naphthalenide have been shown to be effective reagents in the conventional synthesis of **2**.

Scheme 4



As in the case of the synthesis of **1**, our best results have been obtained by adding cold solutions/slurries of $CrCl_3(THF)_3$ to mechanically stirred mixtures of alkali-metal naphthalenides in THF at −60 °C, followed by a slow warmup with continuous stirring. Our results are not optimized, since THF was the only solvent used in the preparation of **2**. However, up to 34% yields of pure $Cr(C_{10}H_8)_2$ have been obtained by the lithium naphthalenide reduction of $CrCl_3(THF)_3$ in THF (eq 2). This

$$CrCl_3(THF)_3 + 3LiC_{10}H_8 \xrightarrow[-60\text{ to }0\text{ °C}]{\text{THF}} \underset{34\%}{Cr(C_{10}H_8)_2} + 3LiCl \quad (2)$$

yield compares favorably with the best ones previously reported for the potassium (36%)[15] and chromium (43%)[5a] atom routes to **2**, although much lower yields of **2**, e.g., 6−7%, have also been reported for the chromium atom synthesis.[5b]

Synthesis of $Mo(C_{10}H_8)_2$ (3). Bis(naphthalene)molybdenum(0) has been previously prepared in 5% and 19% yields by the molybdenum and magnesium atom routes, respectively.[6] The latter involved the condensation of magnesium atoms into a THF mixture of $MoCl_5$ and naphthalene at −110 °C. We have found that conventional lithium naphthalenide reductions of $MoCl_4(THF)_2$ and $MoCl_3(THF)_3$ in THF at low temperature (−60 °C) followed by a slow warm up provided spectroscopically pure **3** in 17% and 20% yields, respectively (Scheme 4). Since $MoCl_3(THF)_3$ is not as easily prepared as $MoCl_4(THF)_2$,[21] the procedure using the latter species is the recommended one. Both methods provide pure **3** in yields that are quite similar to the best yield (19%) previously reported for the magnesium atom synthesis.[6] Only magnetically stirred reaction mixtures have been used in the synthesis of **3**, while our best yields of **1** and **2** were obtained with generally more efficient mechanical stirring. Another indication that our syntheses of **3** are not yet optimized is that only lithium naphthalenide reductions in THF have been carried out to date. Nevertheless, they represent effective and facile routes to a substance whose chemical properties remain poorly explored. Our samples of **3** provide ^1H and ^{13}C NMR spectra in good agreement with those previously reported by Kündig and coworkers.[6] However, as noted in the Experimental Section, a heteronuclear $^1H-^{13}C$ multiple quantum correlation (HMQC) spectrum of **3** established that the previous assignments[6] for the hydrogen resonances corresponding to the unbound naphthalene ring were incorrect. A proton-coupled ^{13}C NMR spectrum of **3** was also obtained to determine previously unreported $^1J_{H-C}$

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[30] Braga, D.; Sabatino, P. *Acta Crystallogr.* **1990**, *C46*, 2308.

[31] Fischer, E. O.; Fritz, H. P.; Manchot, J.; Priebe, E.; Schneider, R. *Chem. Ber.* **1963**, *96*, 1418.

[32] Radonovich, L. J.; Zuerner, E. D.; Edner, H. F.; Klabunde, K. *Inorg. Chem.* **1976**, *15*, 2976.

[33] Brock, C. P.; Dunitz, J. D. *Acta Crystallogr.* **1982**, *B38*, 2218.

values, which range from 159 to 165 Hz. These values are close to those reported for the chromium analog **2**[22] and support prior conclusions that **2** and **3** have very similar molecular structures in solution.

Concluding Comments

We have established that the interaction of conventionally generated alkali-metal naphthalenides with $MCl_3(THF)_3$ (M = V, Cr, Mo) and $MoCl_4(THF)_2$ in THF or DME provided the corresponding bis(naphthalene)metal(0) complexes as isolable species. These highly reactive compounds were obtained in yields that are similar to those previously reported from metal atom syntheses. Our results also confirm for the first time that Henrici-Olivé and Olivé did indeed prepare $V(C_{10}H_8)_2$ in solution over 25 years ago by a standard "wet chemical" technique.[10] Unambiguous characterization of bis(naphthalene)vanadium(0) was provided by a single-crystal X-ray structural characterization, which showed that the vanadium complex has virtually the same structure as that previously established for the chromium analog.[22] Our prior reports on the syntheses of $Ti(arene)_2$ with biphenyl[34] or naphthalene[13] radical anions and the present one establish that this arene radical anion route is of *general utility* in the synthesis of homoleptic (arene)metal(0) complexes, which were previously only available by Fischer–Hafner or metal atom syntheses.[9] Notably, however, the latter methods, save the potassium atom route, cannot be used directly to synthesize corresponding anionic species, such as $[Zr(\eta^4\text{-}C_{10}H_8)_3]^{2-}$.[14,35] In this respect our "radical approach" to homoleptic (arene)metal complexes has proven to be more versatile in certain instances than prior methods. We believe that syntheses of the presently unknown homoleptic (naphthalene)metal(0) complexes of Sc, Zr, Hf, Nb, Ta, W, and Re by the naphthalenide route will be of particular significance. These are now under examination in this laboratory.

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Supporting Information Available: Tables of positional parameters and *B*(eq) values, *U* values, bond lengths and angles, and least-squares planes and atomic deviations therefrom for the X-ray study of **1** (11 pages). Ordering information is given on any masthead page.

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[34] Blackburn, D. W.; Britton, D.; Ellis, J. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1495.

[35] Zenneck, U. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 53.